

# **Report for 2001MN3382B: A Novel in situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate**

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## A novel in-situ technology for the treatment of groundwater contaminated with agriculturally-derived nitrate

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**Project duration:** March 1, 2000 to February 28, 2002

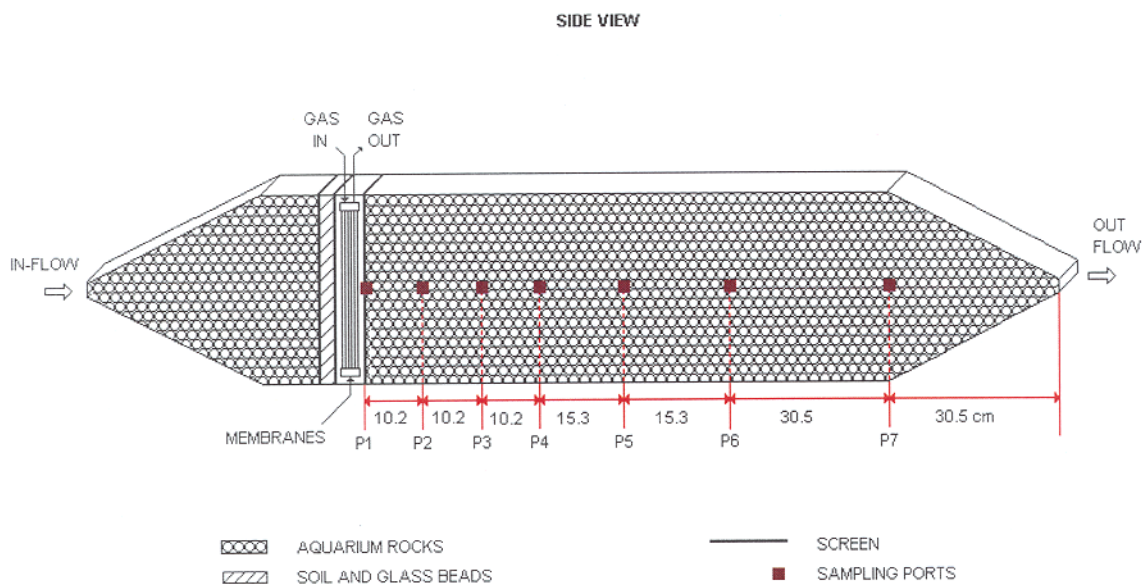
### Summary

A novel *in situ* membrane technology was developed to remove nitrate ( $\text{NO}_3^-$ ) from groundwater. Membrane-fed hydrogen gas ( $\text{H}_2$ ) was used as an electron donor to stimulate denitrification. A flow-through reactor fit with 6 hollow-fiber membranes (surface area =  $93 \text{ cm}^2$ ) was designed to simulate groundwater flowing through an aquifer with a velocity of  $0.3 \text{ m/day}$ . This membrane technology supported excellent  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) removal once  $\text{H}_2$  and carbon limitations were corrected. The membrane module achieved a maximum  $\text{H}_2$  flux of  $1.79 \times 10^{-2} \text{ mg H}_2/\text{m}^2\text{-s}$ , which was sufficient to completely remove  $16.4 \text{ mg/L NO}_3^- \text{-N}$  from a synthetic groundwater with no  $\text{NO}_2^-$  accumulation. In addition, this model *in situ* treatment process produced a high quality water containing less than  $0.5 \text{ mg/L}$  total organic carbon.

### Introduction

The experiments described within this report were designed to evaluate the use of *in situ* hydrogenotrophic denitrification for remediating  $\text{NO}_3^-$ -contaminated groundwaters. Denitrifying bacteria were cultured from soil from the University of Minnesota St. Paul agricultural station. Denitrifying cultures were started June 23, 2000 by adding 50 grams of soil to 100 ml of anoxic synthetic groundwater media. A series of microcosm experiments were performed to develop denitrifying cultures that could use  $\text{H}_2$  to reduce  $\text{NO}_3^-$ .

To evaluate hydrogenotrophic denitrification *in situ* using hollow fiber membranes, a flow-through box reactor was constructed as shown in Figure 1. The box was designed to simulate groundwater flow through an aquifer. The central rectangular test section measured  $2.5 \text{ cm}$  in width,  $1.83 \text{ m}$  in length, and  $0.304 \text{ m}$  deep and was packed with aquarium rocks (Estes' Ultrastone) and soil from the University of Minnesota to simulate *in situ* conditions. Additional tapered inlet and exit sections measuring  $0.3 \text{ m}$  in length were designed to promote uniform flow in the



**Figure 1.** Schematic of flow-through reactor

central test section. The 14.2L reactor was equipped with a removable lid. The lid contained two holes to supply  $H_2$  to the membrane module. The membrane module consisted of six reinforced silicone hollow fiber membranes. Seven gas-tight sampling ports were installed at mid-depth along the length of the reactor for sample collection.

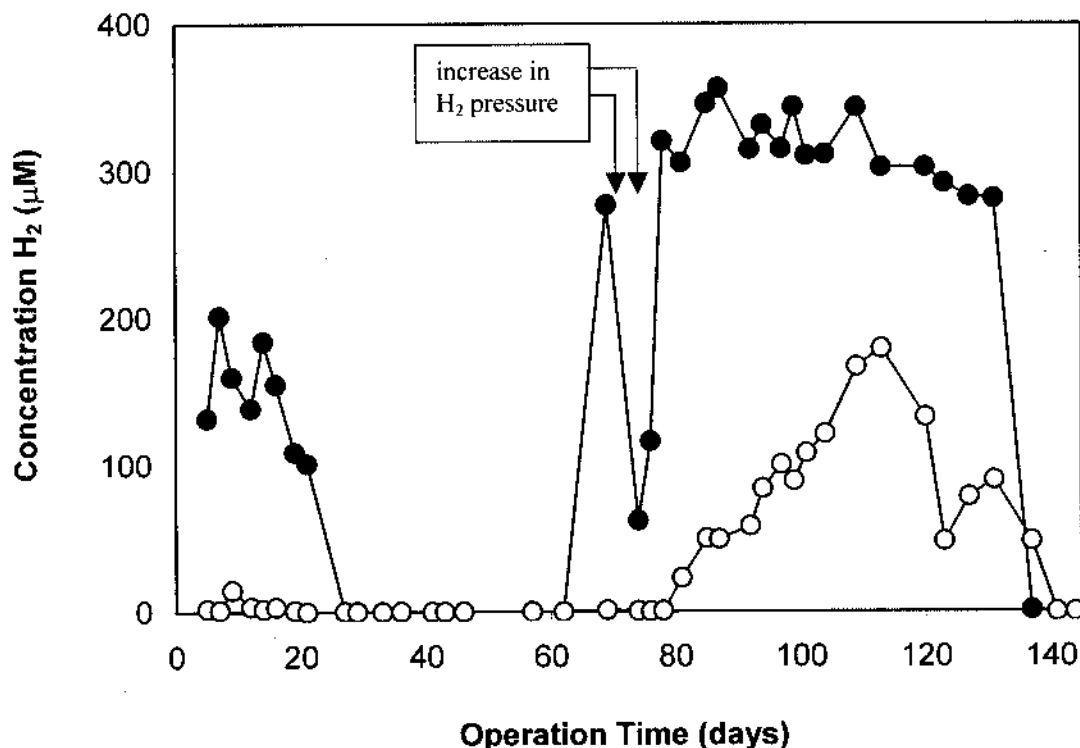
Methylene blue tracer studies were conducted on the box and it was shown that the water moved through the box uniformly in a plug-flow manner.

Prior to the flow-through experiments the reactor was seeded with buffered synthetic groundwater containing an active culture of denitrifying bacteria was allowed to stand for a week. A synthetic, slightly oxic (2 mg  $O_2/L$ ) groundwater flow was then pumped through the reactor at a rate of 1.6 ml/min. For three weeks medium was pumped through the reactor without the addition of  $H_2$ . After three weeks the membrane module was supplied with 100 %  $H_2$  at a gas flowrate of 0.5 ml/min.

Liquid samples were collected weekly from the reactor sample ports P1 – P7. P1 was located 1 cm downgradient of the membranes. P7 was approximately 93 cm downgradient of the membranes.  $NO_3^-$  and  $NO_2^-$  concentrations were measured using ion chromatography. Dissolved  $H_2$  concentrations were determined by gas chromatography. Influent and effluent samples were also analyzed weekly for total organic carbon (TOC), pH, redox potential and protein content.

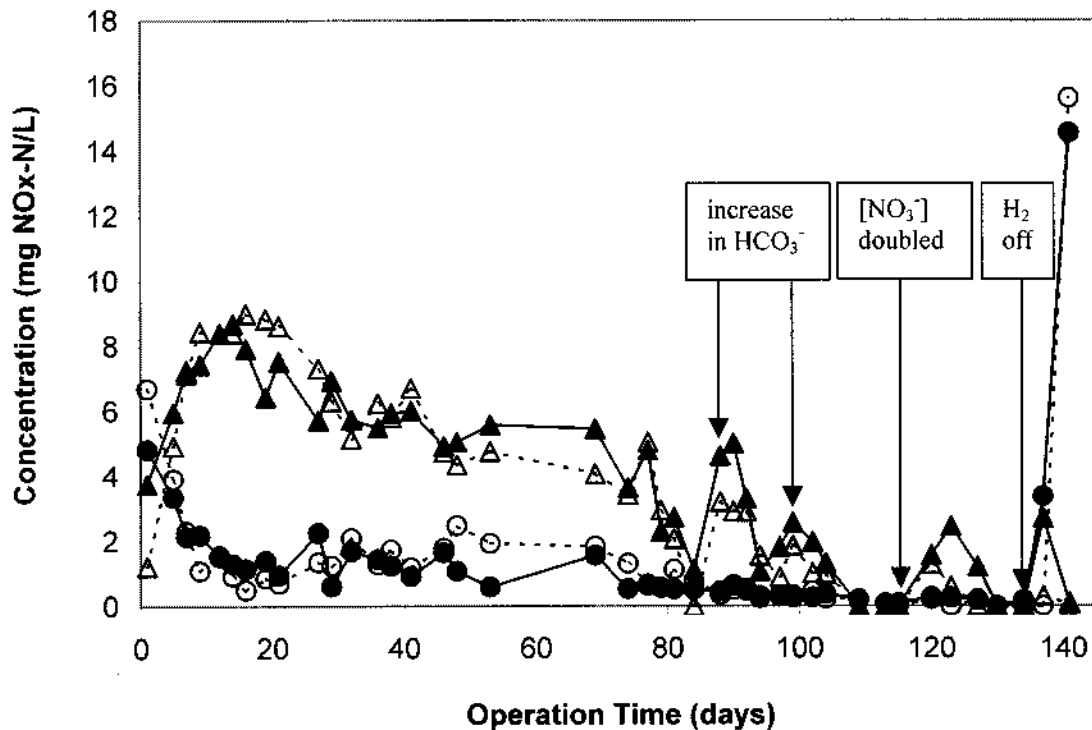
## Results

The study successfully demonstrated that the membrane modules could supply  $H_2$  to groundwater in sufficient concentration to effectively remove  $NO_3^-$  and  $NO_2^-$  at concentrations as high as 16.4 mg N/L. The dissolved  $H_2$  concentration is shown as a function of operating time in Figure 2. The  $H_2$  concentration dropped to very low level between days 25 and 60, indicating that the system was probably  $H_2$ -limited during this period, but after the  $H_2$  gas pressure was elevated to 1.44 atm, high residual dissolved  $H_2$  concentrations were observed.



**Figure 2.** Dissolved  $H_2$  concentration at sampling ports 1 and 7. Symbols are: ● port 1 and ○ port 7.

The reactor required time to develop a microbial population capable of effective  $NO_3^-$  and  $NO_2^-$  removal (Figure 3). Nevertheless, in this study we were able to demonstrate that both  $NO_3^-$  and  $NO_2^-$  were effectively



**Figure 3.** NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentration at sampling ports 1 and 7. Symbols are: ● NO<sub>3</sub><sup>-</sup> at port 1, ○ NO<sub>3</sub><sup>-</sup> at port 7, ▲ NO<sub>2</sub><sup>-</sup> at port 1, △ NO<sub>2</sub><sup>-</sup> at port 7.

removed *in situ* by biological denitrification. The majority of the NO<sub>3</sub><sup>-</sup> degradation occurred within a few centimeters of the membrane module, removing 169 mg N/h per m<sup>2</sup> of membrane. The variability in performance and the time required to achieve full removal was influenced by operating conditions, namely the H<sub>2</sub> pressure and the concentration of HCO<sub>3</sub><sup>-</sup> in the reactor. The system was H<sub>2</sub> and carbon dioxide limited for some time. Once this was recognized and corrected, excellent performance was achieved. This implies that in the field a carbon source (such as carbon dioxide) may need to be added for effective remediation, although in most situations adequate alkalinity (>90 mg/L as CaCO<sub>3</sub>) would be present.

The aquarium rock media in the test reactor provided a support for biological growth as well as filtration capacity. Effluent water analyses indicated that the TOC rose by only about 0.5 mg/L as a result of denitrification. This low effluent TOC likely resulted from soluble microbial products and transported biomass. It is reasonable to expect that the product water would improve even more if it had a longer travel path through real aquifer material, which should be more effective in adsorbing and filtering organic matter and biomass than aquarium rocks.

These results indicate that there is merit in pursuing the use of membranes for the *in situ* injection of H<sub>2</sub> gas as a NO<sub>3</sub><sup>-</sup> remediation technology. The membranes can deliver sufficient H<sub>2</sub> to stimulate *in situ* denitrification in a safe and controlled fashion. In addition, as the denitrified water flows through the aquifer to a water supply well, processes such as filtration, adsorption and continued biological action will serve to improve the water quality further.

### Summary and future research

This seed research project was extremely successful. We were able to demonstrate that the process works effectively and has little impact on groundwater quality. Drs. Novak and Semmens used these early results to apply for follow-on funding from the State of Minnesota, Legislative Commission on Minnesota's Resources. They received \$230,000 in funding in July, 2001 for a field trial. The field trial is currently in progress in Becker Minnesota. The funding obtained from the State of Minnesota was due in part to the successful completion of this WRRI project.

**Publications/ presentations**

Katrina Haugen, a civil engineering graduate student, conducted this research for her MS thesis project. She graduated in June, 2001 after defending her thesis, titled "A Novel *In Situ* Technology for the Treatment of Nitrate Contaminated Groundwater." Her thesis research has been accepted for publication and is currently in press (Haugen, K. S., Semmens, M. J., and Novak, P. J. 2002. "A Novel *In Situ* Technology for the Treatment of Nitrate Contaminated Groundwater." *Water Research*, in press).